

electrically-conductive zinc oxide has a specific electric resistivity of  $1 \times 10^3 \text{ } \Omega \cdot \text{cm}$  or less in flake form.

## [DETAILED DESCRIPTION OF THE INVENTION]

[0001]

[Field of Industrial Application]

The present invention relates to a flake-shaped electrically-conductive zinc oxide. Specifically, the present invention relates to a flake-shaped zinc oxide exhibiting white color and excellent electrical conductivity, and a production method therefor. More specifically, the present invention relates to a flake-shaped electrically-conductive zinc oxide which is capable of being added to various types of resins and coating materials having electrical insulating properties to impart an electrical conductivity thereto, e.g., for the purpose of providing excellent antistatic properties, to IC trays, wrapping materials, coating materials or the like, and further usable as an electrical conductivity-imparting agent for plastic, paper, cloth or the like, and a production method therefor.

[0002]

[Prior Art]

For the purpose of imparting an electrical conductivity to various types of resins and coating materials, an electrically-conductive powder is commonly used as filler. In view of allowing a base material to be freely colored, it is desired to provide a whitish electrically-conductive powder. Recently, for the purpose of allowing an effective electrical conductivity to be imparted in a lower addition amount, it is desired to provide a needle-shaped or high-strength plate-shaped powder. As a technique for meeting such needs, JP 3-28125A discloses "a method which comprises adding sodium hydroxide or potassium hydroxide to a solution containing an alkali metal zincate compound and at least one water-soluble metal compound of a metal selected from the group consisting of tin, gallium, indium and aluminum to have a mole ratio of alkali metal/zinc of 5 to 30 so as to obtain a needle-shaped zinc oxide". JP 3-60429A discloses "a zinc oxide-based electrically-conductive powder which contains a trivalent or tetravalent metal atom in an

amount of 0.0001 to 0.1 moles per mol of Zn atom, wherein a powder particle has a volume resistivity value of  $10^5$   $\Omega$  cm or less, and has a needle shape with an aspect ratio of 3 to 400 or a plate shape with a ratio of length/thickness of 10 to 1000". JP 4-26514A discloses "a method of producing a plate-shaped electrically-conductive zinc oxide, which comprises: preparing an aqueous solution containing 0.5 to 2.0 moles of Zn ion and a trivalent or tetravalent metal atom in an amount of 0.0001 to 0.1 moles per mol of Zn atom, and having a pH of 0.5 to 2.0; adding a base to the aqueous solution in an amount of 0.1 to 4.0 moles per mol of Zn atom while adjusting said aqueous solution to have a pH of 4.0 to 6.5; heating the obtained solution up to a temperature of 80 to 100°C to form a sediment; and burning the sediment under a reducing atmosphere at a temperature of 600 to 1000°C". All the above techniques are intended to add a doping substance, such as Al, Ga or Sn, to a zinc oxide so as to lower a volume resistivity. While each of the techniques achieves an appreciable effect, there is an expectation for emergence of a flake-shaped zinc oxide having a lower volume resistivity value and a high strength.

[0003]

[Problem to be solved by the Invention]

In view of the above circumstances, through various researches for obtaining a flake-shaped zinc oxide having more excellent electrical conductivity while maintaining characteristics of a flake, the inventors found that, when a metal, such as Al or Sn, is added and incorporated to a zinc oxide in a specific manner, a whitish flake-shaped electrically-conductive zinc oxide is obtained with more excellent electrical conductivity as compared with a conventional manner, and when the obtained zinc oxide is burnt in a specific manner, a whitish flake-shaped electrically-conductive zinc oxide having excellent strength as well as an improvement in electrical conductivity is obtained, and have finally accomplished the present invention.

[0004]

[Means for solving the Problem]

Specifically, the present invention provides a flake-shaped electrically-conductive zinc oxide comprising: a flake-shaped zinc oxide which contains aluminum in an amount of

0.0001 to 0.3 moles per mole of zinc atom, and has an average thickness of 0.1 to 2  $\mu\text{m}$ , an average particle size of 1 to 100  $\mu\text{m}$  and an aspect ratio of 3 to 100; and at least one oxide of a metal selected from the group consisting of antimony, indium, cerium, gallium, tin, zirconium and titanium. The oxide is deposited onto a surface of the flake-shaped zinc oxide in an amount of 0.00005 to 0.05 moles per mole of zinc atom.

[0005]

The present invention also provides a method of producing a flake-shaped electrically-conductive zinc oxide, comprising: adding a solution which contains a zinc salt and an aluminum salt in a coexisting state to have aluminum in an amount of 0.0001 to 0.3 moles per mole of zinc atom, and a hexamethylenetetramine solution and/or an urea solution, to hot water in a quantitative ratio of 1 : 1 to induce hydrolysis while maintaining pH in the range of 5.5 to 7.5 so as to produce a flake-shaped basic zinc-based coprecipitation product; adding at least one water-soluble compound of a metal selected from the group consisting of antimony, indium, cerium, tin, zirconium and titanium, to the flake-shaped basic zinc-based coprecipitation product in an amount of 0.00005 to 0.05 moles per mole of zinc atom, so as to be deposited onto a surface layer of the flake-shaped basic zinc-based coprecipitation product; and burning the obtained product under a reducing atmosphere.

[0006]

Further, the present invention provides a method of producing a flake-shaped electrically- conductive zinc oxide, comprising: adding a solution which contains a zinc salt and an aluminum salt in a coexisting state to have aluminum in an amount of 0.0001 to 0.3 moles per mole of zinc atom, and a hexamethylenetetramine solution and/or an urea solution, to hot water in a quantitative ratio of 1 : 1 to induce hydrolysis while maintaining pH in the range of 5.5 to 7.5 so as to produce a flake-shaped basic zinc-based coprecipitation product; separating the flake-shaped basic zinc-based coprecipitation product from a liquid phase; burning the separated flake-shaped basic zinc-based coprecipitation product to form a flake-shaped zinc oxide; adding at least one water-soluble compound of a metal selected from the group consisting of antimony, indium, cerium, tin, zirconium and titanium, to the flake-shaped zinc oxide in an amount of 0.00005 to 0.05 moles per mole of zinc atom, so as

to be deposited onto a surface layer of the flake-shaped zinc oxide; and burning the obtained product under a reducing atmosphere.

[0007]

In the above method of the present invention, the flake-shaped basic zinc-based coprecipitation product after depositing the metal atoms onto the surface layer thereof is preliminarily burnt under an oxidizing atmosphere at a temperature rise rate of 1 to 10°C/minute and at a temperature of 800 to 1000°C for a holding time of 10 minutes to 10 hours, and further burnt under a reducing atmosphere at a temperature of 700 to 850°C for a holding time of 10 minutes to 3 hours.

[0008]

In the above method of the present invention, during the process of burning the flake-shaped basic zinc-based coprecipitation product, depositing the water-soluble compound of the metal onto the obtained flake-shaped zinc oxide, and burning the obtained product under a reducing atmosphere, the burning of the flake-shaped basic zinc-based coprecipitation product is performed under an oxidizing atmosphere at a temperature rise rate of 1 to 10°C/minute and at a temperature of 800 to 1000°C for a holding time of 10 minutes to 10 hours, and the burning under a reducing atmosphere is performed at a temperature of 700 to 850°C for a holding time of 10 minutes to 3 hours.

[0009]

The present invention will be more specifically described below. The flake-shaped electrically-conductive zinc oxide of the present invention comprises: a flake-shaped zinc oxide which contains aluminum in an amount of 0.0001 to 0.3 moles per mole of zinc atom, and has an average thickness of 0.1 to 2  $\mu\text{m}$ , an average particle size of 1 to 100  $\mu\text{m}$  and an aspect ratio of 3 to 100; and at least one oxide of a metal selected from the group consisting of antimony, indium, cerium, gallium, tin, zirconium and titanium. The oxide is deposited onto a surface of the flake-shaped zinc oxide in an amount of 0.00005 to 0.05 moles per mole of zinc atom.

[0010]

Typically, a flake-shaped electrically-conductive zinc oxide is produced by adding a

precipitant to a zinc salt solution to form a flake-shaped basic zinc salt as a precursor to a flake-shaped zinc oxide, and then burning the precursor under a reducing atmosphere. During this process, for the purpose of improving electrical conductivity, a dissimilar metal having a different valence number is incorporated into the zinc oxide as a solid solution to control an atomic valence. It is commonly known to use aluminum as the dissimilar metal. In the present invention, an amount of aluminum existing in the zinc oxide is in the range of 0.0001 to 0.3 moles, preferably 0.001 to 0.1, more preferably 0.005 to 0.05, per mole of zinc atom. If the aluminum atom to the zinc ion is out of the above range, the electrical conductivity will deteriorate. In addition, the aluminum in the present invention exists in the flake-shaped zinc oxide in a uniformly-dispersed state.

[0011]

In the flake-shaped electrically-conductive zinc oxide of the present invention, a flake has a thickness of about 0.1 to 2  $\mu\text{m}$ , preferably about 0.2 to 1.5  $\mu\text{m}$ , and an average size of about 1 to 100  $\mu\text{m}$ , preferably about 5 to 80  $\mu\text{m}$ . If the flake has a thickness of less than the above lower limit, the flake will be broken during use to cause difficulty in maintain a desired shape of the zinc oxide. Conversely, if the flake has a thickness of greater than the above upper limit, the number of flakes per unit weight will be reduced to cause deterioration in an electric conductivity imparting effect or an antistatic effect. If the flake has a size of greater than the above upper limit, the flake will be liable to be broken during use. If the flake has a size of less than the above lower limit, the electric conductivity imparting effect or the antistatic effect as the flake-shaped electrically-conductive zinc oxide will deteriorate.

[0012]

In the present invention, it is essential to deposit at least one oxide of a metal selected from the group consisting of antimony, indium, cerium, gallium, tin, zirconium and titanium, onto a surface of the aluminum-containing flake-shaped zinc oxide, in the form of metal atoms in an amount of about 0.00005 to 0.05 moles, preferably about 0.0001 to 0.03 moles, per mole of zinc atom. Although the reason has not been clarified, even if the above metal is uniformly dispersed in the zinc oxide in the form of an oxide together with aluminum, no electrical-conductivity improving effect can be obtained. If an amount of metal atoms

deposited onto a zinc atom is less than 0.00005 moles, the electrical conductivity is not improved. Conversely, if the metal atoms are deposited onto the zinc oxide in an amount of greater than 0.05 moles, an electrical-conductivity improving effect reflecting an increase in the deposition amount cannot be obtained, and the zinc oxide is likely to be colored depending on the type of metal. Any one of antimony, indium, cerium, gallium, tin, zirconium and titanium can contribute to an improvement in electrical conductivity. Among them, a combination of tin and antimony has superiority in the electrical- conductivity improving effect.

[0013]

As a method of producing the above flake-shaped electrically-conductive zinc oxide of the present invention, one method comprises: adding a solution which contains a zinc salt and an aluminum salt in a coexisting state, and a hexamethylenetetramine solution and/or an urea solution, to hot water in a quantitative ratio of 1 : 1 to induce hydrolysis while maintaining pH in the range of 5.5 to 7.5 so as to produce a flake-shaped basic zinc-based coprecipitation product; adding at least one water-soluble compound of a metal selected from the group consisting of antimony, indium, cerium, tin, zirconium and titanium, to the flake-shaped basic zinc-based coprecipitation product, in the form of metal atoms in an amount of 0.00005 to 0.05 moles per mole of zinc atom, so as to be deposited onto a surface layer of the flake-shaped basic zinc-based coprecipitation product through hydrolysis; and burning the obtained product under a reducing atmosphere. Another method comprises: adding at least one water-soluble compound of a metal selected from the group consisting of antimony, indium, cerium, tin, zirconium and titanium, to a flake-shaped zinc oxide obtained by burning the above flake-shaped basic zinc-based coprecipitation product, in an amount of 0.00005 to 0.05 moles per mole of zinc atom, so as to be deposited onto a surface layer of the flake-shaped zinc oxide through hydrolysis; and burning the obtained product under a reducing atmosphere.

[0014]

The zinc salt to be used in the present invention is not limited to a specific type. For example, a water-soluble zinc salt, such as zinc chloride, zinc sulfate, zinc nitrate or zinc

acetate, may be used. As the aluminum salt, a water-soluble aluminum salt, such as aluminum chloride, aluminum sulfate, aluminum nitrate, aluminum acetate, aluminum phosphate or ammonium alum, may be used. In one embodiment of the present invention, the zinc salt and the aluminum salt are mixed together in an amount of about 0.0001 to 0.3 moles per mole of zinc atom to coexist in a solution.

[0015]

Then, together with a hexamethylenetetramine solution and/or an urea solution, the solution of the coexisting zinc and aluminum salts state is simultaneously added under stirring to hot water at a temperature of about 100°C, in a quantitative ratio of 1 : 1 to induce hydrolysis and neutralization/precipitation reactions while maintaining a reaction pH in the range of about 5.5 to 7.5 so as to obtain flakes in a precipitate flake-shaped basic zinc salt wherein the aluminum is uniformly dispersed in each flake. If the solution of the coexisting zinc and aluminum salts is pre-mixed with a hexamethylenetetramine solution and/or an urea solution to adjust pH to be in the range of about 5.5 to 7.5, and then the mixed solution is poured into hot water to induce hydrolysis so as to obtain a flake-shaped basic zinc salt, the obtained flake-shaped basic zinc salt will exhibit an electric-conductivity imparting effect inferior to that in the process of simultaneously adding the solution of the coexisting zinc and aluminum salts, and a hexamethylenetetramine solution and/or an urea solution, to hot water in a quantitative ratio of 1 : 1 to induce a reaction therebetween, assumingly because the aluminum is not uniformly dispersed in each flake precipitated by the reaction. The hexamethylenetetramine and/or urea serving as a precipitant are used in the range of a stoichiometric value necessary for neutralization of the zinc salt and the aluminum salt, to about five times of the stoichiometric value.

[0016]

The zinc/aluminum salts and the hexamethylenetetramine and/or urea solutions are added to the hot water at a temperature of 100°C for a time of 1 hour or more, typically 2 to 3 hours. Further, a resulting slurry is aged while being kept at the temperature for 1 hour or more, typically 2 to 3 hours, and then cooled down to room temperature or less. The aging may be performed under stirring for a long period of time, e.g., about 24 to 48 hours. This

treatment has an advantage of being able to smooth a flake and uniform a flake size so as to contribute to improvement in yield. With a view to achieving enhanced product yield, after adding the two solutions, the ammonia or the like may be added to adjust the pH of the reaction solution in the range of about 7.5 to 8.1 to perform the aging treatment.

[0017]

Then, the aged solution is subjected to solid-liquid separation, rinsing and drying in a conventional manner to obtain a precursor to a flake-shaped basic zinc sulfate. In this process, a water-soluble organic solvent, such as lower alcohols, polyhydric alcohols, lower esters, tetrahydrofuran or lower ketone, may be added to the reaction solution after the solid-liquid separation so as to dilute the solution and facilitate crystallization, so that further enhanced yield can be obtained, and metal ions in discharged water can be reduced. This water-soluble organic solvent may be added before the solid-liquid separation to contribute to improvement in yield as well as the addition of ammonia.

[0018]

In the present invention, the precursor to a flake-shaped basic zinc sulfate, obtained through the aging treatment in the above process is dried in a conventional manner. Typically, a wet cake after the solid-liquid separation is dispersed in an organic solvent and/or water together with a surfactant, and dried by a spray dryer, drum dryer or the like. Immediately after the drying, or, if necessary, after being preliminarily burnt in a non-reducing atmosphere, the dried precursor is burnt in a reducing atmosphere to produce a flake-shaped electrically-conductive zinc oxide. A preliminary burning temperature and a holding time may be set at conditions allowing hydroxyl groups and acid radicals in the precursor to be thermally decomposed. Typically, the preliminary burning is performed at a temperature of about 800 to 1000°C for a holding time of about 10 minutes to about 10 hours. A usable furnace typically includes a tubular furnace, a box furnace, a kiln furnace and a gas furnace.

°C

[0019]

In the burning under the reducing atmosphere, the atmosphere may include a gas



atmosphere of hydrogen, carbon monoxide or ammonia. The burning may be performed in presence of an auxiliary material, such as urea or carbon, capable of generating the above gas through the burning. A usable carbon may include carbon black, coke, mineral coal and charcoal. The secondary burning of the flake powder is performed at a temperature of about 700 to 850°C for a holding time of about 10 minutes to about 3 hours, preferably about 10 minutes to about 1 hour. If the treatment temperature is less than 700°C, the electrical conductivity cannot be adequately obtained. If the treatment is performed at a temperature of greater than 850°C, a separation of metal zinc is accelerated to cause deterioration in yield and strength. In order to maintain the reducing atmosphere and/or non-oxidizing atmosphere after the burning, the atmosphere is cooled down to room temperature while introducing an inert gas, such as nitrogen or argon, therein. In the above manner, a flake-shaped zinc oxide is obtained in such a manner that the aluminum is uniformly dispersed in each flake.

[0020]

In the present invention, in the preliminary burning of the precursor (flake-shaped basic zinc-based coprecipitation product), the preliminary burning is performed under an oxidizing atmosphere at a temperature rise rate of about 1 to 10°C/minute, preferably about 1 to 3°C/minute and at a temperature of about 800 to 1000°C for a holding time of about 10 minutes to about 10 hours. Then, after the preliminary burning, the secondary burning is performed under a reducing atmosphere at a temperature of about 700 to 850°C. The above conditions of the preliminary burning are particularly recommended to provide a flake-shape electrically- conductive zinc oxide with excellent strength as well as electrical conductivity. Although it has not been clarified why the strength of the burnt flake is improved by performing the preliminary burning in an oxidizing atmosphere under the above conditions before the secondary burning in the reducing atmosphere, it is assumed that the thermal decomposition of hydroxyl groups and acid radicals in the precursor is slowly developed, and therefore the precursor can be burnt without causing deformation and breakup of crystals thereof.

[0021]

In the present invention, after obtaining the flake-shaped zinc oxide precursor in the above process, or a flake-shaped zinc oxide in the subsequent process, at least one or at least metal compound of a metal selected from the group consisting of antimony, indium, cerium, gallium tin, zirconium and titanium, is added in the form of a metal salt solution to the flake-shaped zinc oxide precursor or the flake-shaped zinc oxide in an amount of 0.00005 to 0.05 moles per mole of zinc atom, so as to coat a surface of the flake-shaped zinc oxide or the precursor in the form of a hydroxide through hydrolysis, and then the obtained product is burnt under a reducing atmosphere.

[0022]

The water-soluble compound of the metal material is not limited to a specific type. Typically, the water-soluble compound may include sulfate salts, nitrate salts, halides, salts of organic acids and alkoxides of the metals, such as antimony chloride, antimony fluoride, antimony isopropoxide, indium nitrate, indium sulfate, indium chloride, indium bromide, indium isopropoxide, cerium nitrate, cerium chloride, cerium sulfate, cerium acetate, cerium isopropoxide, gallium nitrate, gallium sulfate, gallium isopropoxide, stannous sulfate, stannic sulfate, stannous fluoride, stannic fluoride, stannous chloride, stannic chloride, stannic iodide, tin isopropoxide, zirconium sulfate, zirconium oxychloride, zirconium isopropoxide, titanium sulfate, titanyl sulfate, titanium chloride and titanium isopropoxide. Each of these compounds may be used after being dissolved in water or an appropriately diluted acid, such as hydrochloric acid, sulfuric acid, nitric acid or acetic acid, or in a water-soluble alcohol, such as methanol, ethanol or isopropanol.

[0023]

Before performing the coating, a soluble salt of antimony or tin, may be added to the slurry solution after the aging in the process for obtaining the flake-shaped zinc oxide precursor, and then an alkali substance, such as ammonia, may be added to finely adjust pH. It is understood that, if the aged slurry solution has a relatively high pH, only the soluble salt may be added. The pH of the slurry solution is finally adjusted in the range of about 7.5 to 8.1. The water-soluble compound may be added in such a manner as to be uniformly dispersed in the solution. Typically, the water-soluble compound is preferably added, but

not limited to, under stirring at a speed of about 0.5 to 10 ml. In order to terminate the hydrolysis reaction of the added metal, an aging treatment after addition is preferably performed at room temperature or under heating, for about 1 hour. The coating process may be performed plural times.

[0024]

The flake-shaped zinc oxide or the lake-shaped zinc oxide precursor having a surface coated with at least one oxide of a metal selected from the group consisting of antimony, indium, cerium, gallium tin, zirconium and titanium, is preliminarily burnt in a non-reducing to oxidizing atmosphere, and then burnt in a reducing atmosphere to obtain a flake-shaped zinc oxide. In this process, the preliminary and secondary burnings may be performed under the same conditions as those in the aforementioned aluminum-containing flake-shaped zinc oxide precursor.

[0025]

[Effect of the Invention]

As mentioned in detail above, the present invention makes it possible to provide a high-strength, whitish flake-shaped zinc oxide exhibiting a high electrical conductivity based on a specific electric resistivity of less than  $2.0 \times 10^2 \Omega \cdot \text{cm}$ . The flake-shaped zinc oxide can be suitably used as an electrical conductivity imparting material, e.g., for: plastic materials requiring antistatic properties, such as an IC tray, a wrapping material and a coating material; data sheets, such as a general recording sheet and a facsimile recording sheet based on electrostatic recording, current-applying recording and electric discharge recording; and other materials, such as a fiber and a fabric, requiring antistatic properties. Thus, the present invention is industrially significantly variable.

[0026]

[Embodiment]

The present invention will be more specifically described based on Examples. In a flake used in Inventive Examples and Comparative Examples, an average particle size was calculated as an average of values of (maximum diameter + minimum diameter) / 2 of 100 flakes. A specific electrical resistivity of an electrically-conductive powder was measured

in a room at a temperature of 23°C and a humidity of 60% RH or less. A surface resistance of the powder was measured by placing a measurement cell in a silica-gel desiccator at 23°C. A sample was adjusted in the following manner.

[0027]

Measurement of Specific Electrical Resistivity: 1g of powder sample was put in an insulated cylinder having a support and a piston for a copper electrode, and the cylinder was pressurized at 100 kg/cm<sup>2</sup>. A contact resistance and a total resistance of the electrode were measured using a multimeter (VPAC 7413/Iwatsu Electric. Co., Ltd.), and a thickness of the sample was measured using a micrometer. Then, the specific electrical resistivity was calculated by the following formula:

Specific electrical resistivity (Ω · cm) = [(total resistance – contact resistance)] × cylinder cross-sectional area (cm<sup>2</sup>) / sample thickness (cm)

[0028]

Measurement of Surface Resistance 1: 0.16g of powder sample was mixed and sufficiently kneaded with 1g of aqueous solution of 7.5 weight% of polyvinyl alcohol (polymerization degree: about 500/produced by Wako Pure Chemical Industries, Ltd.), and dispersed in the solution through a supersonic treatment. Then, the mixture was applied onto a flame-resistant sheet (produced by Kishu Paper Co., Ltd.) using an applicator with a doctor blade having a thickness of 100 μm, and subjected to drying to prepare an electrically-conductive data sheet. A surface resistance of the obtained electrically-conductive data sheet was measured using a 16008A measurement cell/4329A high resistance meter (produced by Yokogawa-Hewlett Packard Ltd.) and a 16008A measurement cell/the above multimeter.

[0029]

Measurement of Surface Resistance 2: 1.03 g of compound consisting of 100 weight parts of polyvinyl chloride resin power (paste resin PQHW: polymerization degree: about 1600 / Sumitomo Chemical Co., Ltd.), 60 weight parts of di-2-ethylhexyl phthalate (produced by Wako Pure Chemical Industries, Ltd.) and 3 weight parts of stabilization agent (Ac-111/ADECA Co.) was kneaded. 1.17 g of powder sample was added to the compound

together with an appropriate amount of ethyl alcohol, and dispersed in the compound through kneading. Then, the mixture was applied onto a release sheet (Osaka Kamibako Co., Ltd.) using an applicator with a doctor blade having a thickness of 200  $\mu\text{m}$ , and subjected to drying at 150°C for 20 minutes to form a film. The film was peeled to prepare an electrically-conductive polyvinyl chloride film. A surface resistance of the obtained electrically-conductive film was measured using the 16008A measurement cell/4329A high resistance meter (produced by Yokogawa- Hewlett Packard Ltd.) and the 16008A measurement cell/the multimeter.

[0030]

Measurement of Strength: 0.5 g of powder sample was dispersed in 100 ml of aqueous solution of 0.2% sodium hexametaphosphate using a homogenizer (US-300Tg: ultrasonic disperser/produced by Leeds & Northrup Co.) for 1 minute and for 10 minutes, and an average particle size of each flake after the two treatments was measured. Then, the strength of the flake was calculated by the following formula:

(Average particle size after 10-minute dispersion treatment / average particle size after 1-minute dispersion treatment)  $\times$  100%

[0031]

#### INVENTIVE EXAMPLE 1

86.7 g of zinc sulfate heptahydrate ( $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ /produced by Wako Pure Chemical Industries, Ltd.) and 0.95 g of aluminum sulfate hydrate ( $\text{Al}_2(\text{SO}_4)_3 \cdot 14 \text{ to } 18 \text{ H}_2\text{O}$ /produced by Wako Pure Chemical Industries, Ltd.) were dissolved in deionized water under heating to prepare 140 ml of solution. 2.2g of hexamethylenetetramine ( $\text{C}_6\text{H}_{12}\text{N}_4$ /produced by Wako Pure Chemical Industries, Ltd.) and 35.2 g of urea ( $(\text{NH}_2)_2 \text{CO}$ /produced by Wako Pure Chemical Industries, Ltd.) were dissolved in the same manner to prepare 140 ml of solution. 20 ml of deionized water was poured into a 500 ml separable flask, and heated up to about 98 to 100°C under stirring using a stirring paddle blade to obtain hot water. Each of the prepared solutions was concurrently poured into the hot water using double micro-tube pump at a preparation volume ratio (flow ratio of 140 volume parts/140 volume parts) by taking two hours. A reaction slurry after 30 minutes from the initiation of the concurrent pouring

had a pH of about 5.7. After the completion of the concurrent pouring, the solution was continuously heated under stirring to keep an aging temperature at about 100 to 102°C for 2 hours. Then, the solution was cooled down to 10°C which is less than room temperature, and 25% ammonia water was added to the solution to adjust the pH from about 6.3 to about 8.1. Then, the solution was further aged under stirring for 2 hours.

[0032]

Then, 0.37 g of stannous chloride dihydrate ( $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ /produced by Wako Pure Chemical Industries, Ltd.) and 0.034 g of antimony chloride ( $\text{SbCl}_3$ /produced by Wako Pure Chemical Industries, Ltd.) were pre-dissolved in two predetermined hydrochloric acid solution under heating, and 15 ml of the prepared solution was poured into the aged solution under stirring by taking about 15 minutes. Then, the solution was further aged for 1 hour. After the aging, the solution has a pH of about 7.8. The prepared flake-shaped precursor slurry was subjected to solid-liquid separation, rinsing with 300 ml of deionized water and substitution with 50 ml of ethyl alcohol. Then, the ethyl alcohol was subjected to an ultrasonic dispersion treatment for 1 hour, and drying with a spray dryer to obtain 38.3 g of flake-shaped precursor.

[0033]

3.15 g of the obtained flake-shaped precursor was placed in a box furnace. The flake-shaped precursor was heated at a temperature rise rate of 100°C/hour, and preliminarily burnt at a temperature of 950°C  $\times$  5 hours. Then, together with 2g of charcoal, the burnt product was transferred to a tube furnace having an air seal system with a bubbling function. The product was heated at a temperature rise rate of 200°C/hour, and burnt at a temperature of 800°C  $\times$  0.5 hours. Then, nitrogen gas was introduced into the tube furnace while preventing an internal pressure of the tube furnace from being reduced, to cool the product to room temperature so as to produce 2.0 g of flake-shaped electrically-conductive zinc oxide.

[0034]

The obtained flakes had a thickness of about 0.2  $\mu\text{m}$ , an average particle size of 7  $\mu\text{m}$ , and a yield of 96%. A specific electrical resistivity, a surface resistance and a strength of the flake were measured as follows: specific electrical resistivity =  $6.7 \times 10^0 \text{ O} \cdot \text{cm}$ ; surface

resistance 1 =  $6.4 \times 10^5 \text{ O}$ ; surface resistance 2 =  $7.2 \times 10^5 \text{ O}$ ; and strength = 81%. Further, as a result of a fluorescent X-ray analysis on Zn, Al, Sn and Sb of the flake, proportions of aluminum, tin and antimony were 0.01 moles, 0.005 moles and about 0.0005 moles per mole of zinc atom, respectively.

[0035]

#### INVENTIVE EXAMPLE 2

Except that the hexamethylenetetramine and urea in Inventive Example 1 were substituted with 44.4 g of hexamethylenetetramine, a flake-shaped electrically-conductive zinc oxide was produced in the same manner. The obtained flakes had a thickness of about 0.2  $\mu\text{m}$ , an average particle size of 7  $\mu\text{m}$ , and a yield of 98%. A specific electrical resistivity, a surface resistance and a strength of the flake were measured as follows: specific electrical resistivity =  $1.1 \times 10^1 \text{ O} \cdot \text{cm}$ ; surface resistance 1 =  $5.7 \times 10^5 \text{ O}$ ; surface resistance 2 =  $8.1 \times 10^5 \text{ O}$ ; and strength = 79%. Further, as a result of a fluorescent X-ray analysis on Zn, Al, Sn and Sb of the flake, proportions of aluminum, tin and antimony were 0.01 moles, 0.05 moles and about 0.005 moles per mole of zinc atom, respectively.

[0036]

#### COMPARATIVE EXAMPLE 1

Except that the obtained precursor in Inventive Example 2 was not subjected to the surface-layer coating by tin-antimony, the precursor was precipitated, dispersed and dried in the same manner to obtain 34 g of flake-shaped precursor. Then, 3.5 g of the precursor and 2.5 g of urea were placed in a tube furnace having a nitrogen seal system with a bubbling function. The precursor was heated at a temperature rise rate of 200°C/hour, and burnt at a temperature of 800°C  $\times$  30 minutes. Then, nitrogen gas was introduced into the tube furnace while preventing an internal pressure of the tube furnace from being reduced, to cool the burnt product to room temperature so as to produce 2.25 g of flake-shaped electrically-conductive zinc oxide. The obtained flakes had a thickness of about 0.2  $\mu\text{m}$ , an average particle size of 7  $\mu\text{m}$ , and a yield of 98%. A specific electrical resistivity, a surface resistance and a strength of the flake were measured as follows: specific electrical resistivity =  $2.1 \times 10^2 \text{ O} \cdot \text{cm}$ ; surface resistance 1 =  $9.0 \times 10^5 \text{ O}$ ; surface resistance 2 =  $4.5 \times 10^5 \text{ O}$ ; and

strength = 52%. Further, as a result of a fluorescent X-ray analysis on Zn and Al of the flake, proportion of aluminum was 0.01 moles, per mole of zinc atom.

[0037]

#### INVENTIVE EXAMPLE 3

Except that 0.37 g of stannous chloride dihydrate was substituted with stannic chloride hydrate ( $\text{SnCl}_4 \cdot n\text{H}_2\text{O}$ /produced by Wako Pure Chemical Industries, Ltd.), and 0.034 g of antimony chloride was changed to 0.35 g of antimony chloride, a flake-shaped electrically-conductive zinc oxide was produced in the same manner. The obtained flakes had a thickness of about 0.2  $\mu\text{m}$ , an average particle size of 7  $\mu\text{m}$ , and a yield of 98%. A specific electrical resistivity, a surface resistance and a strength of the flake were measured as follows: specific electrical resistivity =  $1.4 \times 10^1 \Omega \cdot \text{cm}$ ; surface resistance 1 =  $4.1 \times 10^5 \Omega$ ; surface resistance 2 =  $7.8 \times 10^5 \Omega$ ; and strength = 61%. Further, as a result of a fluorescent X-ray analysis on Zn, Al, Sn and Sb of the flake, proportions of aluminum, tin and antimony were 0.01 moles, 0.05 moles and about 0.005 moles per mole of zinc atom, respectively.

[0038]

#### INVENTIVE EXAMPLE 4

Except that stannous chloride dihydrate and the antimony chloride in Inventive Example 2 was substituted with 0.092 g of stannic sulfate ( $\text{Sn}(\text{SO}_4)_2$ : produced by Kishida Chemical Co., Ltd.), and changed in amount to 0.0069 g, and dissolved in 15 ml of 1 mole/l sulfuric acid aqueous solution under heating, a flake-shaped electrically-conductive zinc oxide was produced in the same manner. The obtained flakes had a thickness of about 0.2  $\mu\text{m}$ , an average particle size of 7  $\mu\text{m}$ , and a yield of 98%. A specific electrical resistivity, a surface resistance and a strength of the flake were measured as follows: specific electrical resistivity =  $1.5 \times 10^2 \Omega \cdot \text{cm}$ ; surface resistance 1 =  $7.1 \times 10^6 \Omega$ ; surface resistance 2 =  $2.2 \times 10^6 \Omega$ ; and strength = 76%. Further, as a result of a fluorescent X-ray analysis on Zn, Al, Sn and Sb of the flake, proportions of aluminum, tin and antimony were 0.01 moles, about 0.001 moles and about 0.0001 moles per mole of zinc atom, respectively.

[0039]

#### INVENTIVE EXAMPLE 5



Except that the stannous chloride dihydrate and the antimony chloride in Inventive Example 2 were substituted, respectively, with 0.87 g of zinc sulfide heptahydrate, and gallium nitrate octahydrate ( $\text{Ga}(\text{NO}_3)_3 \cdot 8\text{H}_2\text{O}$ /produced by Wako Pure Chemical Industries, Ltd.), and dissolved in water, a flake-shaped electrically-conductive zinc oxide was produced in the same manner. The obtained flakes had a thickness of about 0.2  $\mu\text{m}$ , an average particle size of 7  $\mu\text{m}$ , and a yield of 98%. A specific electrical resistivity, a surface resistance and a strength of the flake were measured as follows: specific electrical resistivity =  $1.5 \times 10^2 \text{ O} \cdot \text{cm}$ ; surface resistance 1 =  $7.4 \times 10^6 \text{ O}$ ; surface resistance 2 =  $2.5 \times 10^6 \text{ O}$ ; and strength = 75%. Further, as a result of a fluorescent X-ray analysis on Zn, Al and Ga of the flake, proportions of aluminum and gallium were 0.01 moles and 0.00005 moles per mole of zinc atom, respectively.

[0040]

#### INVENTIVE-EXAMPLE 6

Except that the stannous chloride dihydrate and the antimony chloride in Inventive Example 2 were substituted, respectively, with 1.09 g of titanium sulfide hydrate ( $\text{Ti}(\text{SO}_4)_2 \cdot n\text{H}_2\text{O}$ /produced by Kishida Chemical Co., Ltd.) and 0.0049 g of indium sulfide heptahydrate ( $\text{In}_2(\text{SO}_4)_3 \cdot 7\text{H}_2\text{O}$ /produced by Wako Pure Chemical Industries, Ltd.), and dissolved in 15 ml of 1 mole/l sulfuric acid aqueous solution under heating, a flake-shaped electrically-conductive zinc oxide was produced in the same manner. The obtained flakes had a thickness of about 0.2  $\mu\text{m}$ , an average particle size of 7  $\mu\text{m}$ , and a yield of 98%. A specific electrical resistivity, a surface resistance and a strength of the flake were measured as follows: specific electrical resistivity =  $1.6 \times 10^2 \text{ O} \cdot \text{cm}$ ; surface resistance 1 =  $7.6 \times 10^6 \text{ O}$ ; surface resistance 2 =  $2.3 \times 10^6 \text{ O}$ ; and strength = 75%. Further, as a result of a fluorescent X-ray analysis on Zn, Al, Ti and In of the flake, proportions of aluminum, titanium and indium were 0.01 moles, about 0.01 moles and 0.00005 moles per mole of zinc atom, respectively.

[0041]

#### INVENTIVE EXAMPLE 7

Except that the stannous chloride dihydrate and the antimony chloride in Inventive

Example 2 were substituted, respectively, with 0.69 g of zirconium oxychloride octahydrate ( $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ /produced by Wako Pure Chemical Industries, Ltd. 99%) and 0.0073 g of cerium nitrate hexahydrate ( $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ /produced by Wako Pure Chemical Industries, Ltd.), and dissolved in 15 ml of 1 mole/l sulfuric acid aqueous solution, a flake-shaped electrically-conductive zinc oxide was produced in the same manner. The obtained flakes had a thickness of about 0.2  $\mu\text{m}$ , an average particle size of 7  $\mu\text{m}$ , and a yield of 98%. A specific electrical resistivity, a surface resistance and a strength of the flake were measured as follows: specific electrical resistivity =  $1.5 \times 10^2 \text{ } \Omega \cdot \text{cm}$ ; surface resistance 1 =  $7.4 \times 10^6 \text{ } \Omega$ ; surface resistance 2 =  $2.4 \times 10^6 \text{ } \Omega$ ; and strength = 75%. Further, as a result of a fluorescent X-ray analysis on Zn, Al, Zr and Ce of the flake, proportions of aluminum, zirconium and cerium were 0.01 moles, about 0.07 moles and 0.00006 moles per mole of zinc atom, respectively.

[0042]

#### INVENTIVE EXAMPLE 8

An amount of aluminum sulfate hydrate was changed to 1.9 g, a flake-shaped precursor was precipitated in the same manner. A reaction slurry after 30 minutes from the initiation of the concurrent pouring was sampled and analyzed. The slurry had a pH of about 5.8. Three flakes were collected from the slurry. As a result of SEM-EDX (Scanning Electron Microscope-Energy Dispersive X-ray Microanalyzer) of surfaces of the flakes, Al was equally detected from the flake surfaces.

[0043]

#### INVENTIVE EXAMPLE 9

Except that the flake-shaped precursor obtained in Inventive Example 1 was placed in a ring furnace, wherein the precursor was preliminarily burnt at a temperature of  $775^\circ\text{C} \times 3$  hours after being heated at a temperature rise rate of  $100^\circ\text{C}/\text{hour}$ , and burnt at a temperature of  $1000^\circ\text{C} \times 5$  hours after being successively heated at a temperature rise rate of  $200^\circ\text{C}/\text{hour}$ , a flake-shaped electrically-conductive zinc oxide was produced in the same manner. The obtained flakes had a thickness of about 0.2  $\mu\text{m}$ , an average particle size of 7  $\mu\text{m}$ , and a yield

of 98%. A specific electrical resistivity, a surface resistance and a strength of the flake were

measured as follows: specific electrical resistivity =  $1.5 \times 10^1 \text{ O} \cdot \text{cm}$ ; surface resistance 1 =  $7.4 \times 10^6 \text{ O}$ ; surface resistance 2 =  $2.4 \times 10^6 \text{ O}$ ; and strength = 73%.

[0044]

#### COMPARATIVE EXAMPLE 2

Except that 20 ml of water in the 500 ml separable flask in Inventive Example 1 was substituted with 160 ml of solution of zinc sulfate heptahydrate and aluminum sulfate, wherein the solution was heated up to about 100°C, and an aqueous precipitant solution (hexamethylenetetramine and urea) was added thereto under stirring, a precursor was produced in the same manner, i.e., through the aging at a high temperature, the pH fine adjustment using ammonia and the low-temperature aging. Subsequently, except that the coating treatment was not performed, a faintly-yellow flake-shaped electrically-conductive zinc oxide was produced in the same manner, i.e., through the dispersion, the drying, the preliminary burning and the secondary burning under the reducing atmosphere. The obtained flakes had a thickness of about 0.5  $\mu\text{m}$ , an average particle size of 17  $\mu\text{m}$ , and a yield of 98%. A specific electrical resistivity, a surface resistance and a strength of the flake were measured as follows: specific electrical resistivity =  $2.7 \times 10^3 \text{ O} \cdot \text{cm}$ ; surface resistance 1 =  $1.8 \times 10^8 \text{ O}$ ; surface resistance 2 =  $1.3 \times 10^8 \text{ O}$ ; and strength = 61%. Further, as a result of a fluorescent X-ray analysis on Zn and Al of the flake, a proportion of aluminum was 0.01 moles per mole of zinc atom. A reaction slurry after 30 minutes from the initiation of the concurrent pouring was sampled and analyzed. The slurry had a pH of about 5.3.

[0045]

#### COMPARATIVE EXAMPLE 3

Except that 20 ml of water in the 500 ml separable flask in Inventive Example 1 was substituted with 300 ml of solution (pH = about 3; if pH = 4 or more, precipitation will occurs) prepared by dissolving zinc sulfate heptahydrate, aluminum sulfate and precipitant in dilute sulfuric acid, wherein the solution was heated up to about 98 to 100°C, a precursor was precipitated in the same manner, i.e., through the aging at a high temperature, the pH fine adjustment using ammonia and the low-temperature aging. Subsequently, except that the coating treatment was not performed, a flake-shaped electrically-conductive zinc oxide was

produced in the same manner, i.e., through the dispersion, the drying, the preliminary burning and the secondary burning under the reducing atmosphere. The obtained flakes had a thickness of about 1  $\mu\text{m}$ , an average particle size of 50  $\mu\text{m}$ , and a yield of 97%. A specific electrical resistivity, a surface resistance and a strength of the flake were measured as follows: specific electrical resistivity =  $4.7 \times 10^3 \text{ } \Omega \cdot \text{cm}$ ; surface resistance 1 =  $2.8 \times 10^8 \text{ } \Omega$ ; surface resistance 2 =  $3.1 \times 10^8 \text{ } \Omega$ ; and strength = 53%. Further, as a result of a fluorescent X-ray analysis on Zn and Al of the flake, a proportion of aluminum was 0.01 moles per mole of zinc atom. A reaction slurry after 30 minutes from the initiation of the concurrent pouring was sampled and analyzed. The slurry had a pH of about 5.3.

[0046]

#### COMPARATIVE EXAMPLE 4

20 ml of water in the 500 ml separable flask in Inventive Example 2 was substituted with 200 ml of solution prepared by dissolving zinc sulfate heptahydrate and aluminum sulfate in dilute sulfuric acid. The solution had a pH of 0.7. When 100 g of separately-prepared aqueous precipitant solution was mixed with the raw material solution, a precipitation product was created. The aqueous precipitant solution has a pH of 5.4. Then, the solution was heated up to about 98 to 100°C, and a precursor was prepared in the same manner, i.e., through, the aging at a high temperature, the pH fine adjustment using ammonia and the low-temperature aging. Subsequently, except that the coating treatment was not performed, a flake-shaped electrically-conductive zinc oxide was produced in the same manner, i.e., the dispersion, the drying, the preliminary burning and the secondary burning under the reducing atmosphere. The obtained flakes had a thickness of about 0.2  $\mu\text{m}$ , an average particle size of 10  $\mu\text{m}$  (however, a great number of fine particles having particle size of 1  $\mu\text{m}$  or less were included), and a yield of 97%. A specific electrical resistivity, a surface resistance and a strength of the flake were measured as follows: specific electrical resistivity =  $4.7 \times 10^3 \text{ } \Omega \cdot \text{cm}$ ; surface resistance 1 =  $2.8 \times 10^8 \text{ } \Omega$ ; surface resistance 2 =  $3.1 \times 10^8 \text{ } \Omega$ ; and strength = 63%. Further, as a result of a fluorescent X-ray analysis on Zn and Al of the flake, a proportion of aluminum was 0.01 moles per mole of zinc atom. A reaction slurry after 30 minutes from the initiation of the concurrent pouring was sampled and

analyzed. The slurry had a pH of about 5.6.

[0047]

#### COMPARATIVE EXAMPLE 5

In Inventive Example 8, zinc salt and aluminum salt as raw materials were dissolved in the water of the separable flask to form 160 ml of solution, and the solution was heated and kept at about 100°C. Then, only 140 ml of precipitant solution was added to the solution under stirring. A reaction slurry after 30 minutes from the initiation of the addition was sampled and analyzed. The slurry had a pH of about 5.4. Three flakes were collected from the slurry. As a result of SEM-EDX (Scanning Electron Microscope-Energy Dispersive X-ray Microanalyzer) of surfaces of the flakes, no Al was detected from the flake surfaces.

[0048]

#### INVENTIVE EXAMPLE 10

The flake-shaped precursor obtained in Inventive Example 1 was heated at a temperature rise rate of 20°C/minute, and burnt at a temperature of 1000°C × 1 hour. Then, a flake-shaped electrically-conductive zinc oxide was produced through the reducing treatment in the same manner. The obtained flakes had a thickness of about 0.3 μm, an average particle size of 7 μm, and a yield of 96%. A specific electrical resistivity, a surface resistance and a strength of the flake were measured as follows: specific electrical resistivity =  $6.1 \times 10^1 \Omega \cdot \text{cm}$ ; surface resistance 1 =  $6.3 \times 10^7 \Omega$ ; surface resistance 2 =  $7.3 \times 10^7 \Omega$ ; and strength = 52%.

[0049]

#### INVENTIVE EXAMPLE 11

In Inventive Example 1, the burning in a reducing atmosphere after the preliminary burning was performed at the same temperature rise rate and a burning temperature of 8000°C × 1.5 hours to produce a flake-shaped electrically-conductive zinc oxide. The obtained flakes had a thickness of about 0.2 μm, an average particle size of 7 μm, and a yield of 96%. A specific electrical resistivity, a surface resistance and a strength of the flake were measured as follows: specific electrical resistivity =  $6.1 \times 10^0 \Omega \cdot \text{cm}$ ; surface resistance 1 =  $6.3 \times 10^7 \Omega$ ; surface resistance 2 =  $7.3 \times 10^7 \Omega$ ; and strength = 62%.